

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Oil-Soluble Metal Sulfonates and Lubricants containing them

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns oil-soluble metal salts of hydrocarbon sulfonic acids, said salts being used as detergents and dispersants in lubricating oils and particularly in mineral lubricating oils. The invention also concerns a process for preparing alkaline earth metal hydrocarbon sulfonates and hydrocarbon compositions containing the said sulfonate salts.

It is known to employ alkaline earth metal sulfonates as additives for lubricants, especially those designed for heavy duty service in internal combustion engines. Lubricating oils containing alkaline earth metal sulfonates have an improved detergent action on the parts of the engines that they lubricate and are capable of being used under severe conditions of load and temperature where they prevent the sticking of rings and pistons which would otherwise result from the formation of varnish.

The metal salts of sulfonic acids that have been used in the prior art as detergent additives for lubricants are of two types; namely, salts of petroleum sulfonic acid acids and salts of synthetic sulfonic acids. Petroleum sulfonates that are generally used in lubricating and other oil compositions are derived from high molecular weight sulfonic acids, the latter being produced by the treatment of petroleum oils of the lubricating oil range with fuming sulfuric acid. These sulfonic acids generally have molecular weights of about 300 to 1200,

although salts of sulfonic acids having higher molecular weights, e.g. 2000, are also useful in some applications. More generally, the sulfonic acids whose metal salts are employed in crankcase lubricants have molecular weights in the range of about 400 to 800. Synthetic sulfonates are derived from relatively pure alkyl aryl sulfonic acids having usually more than 10 carbon atoms per molecule. For example, sulfonated products of alkylated aromatics such as benzene, toluene, xylene, and naphthalene, alkylated with olefins or olefin polymers of the type of polypropylene, polyisobutylene, etc. can be used. Calcium sulfonates are generally preferred for lubricating compositions because of their lower ash content. Calcium sulfonates will generally contain about 2 to 5 wt.% calcium, whereas barium sulfonates will generally contain about 10 to 20 wt.% barium.

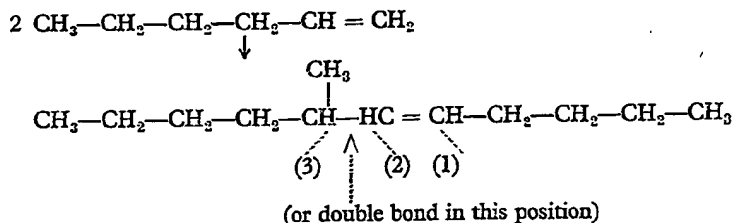
It has now been found that an alkaline earth sulfonate having superior detergent and varnish preventing properties can be prepared by dimerizing a monoolefin fraction in the C<sub>8</sub> to C<sub>15</sub> range by contacting said fraction with an activated silica-alumina catalyst having a silica-to-alumina weight ratio of from 1:1 to 15:1, said contacting being conducted at a temperature in the range of 200 to 500°F at a pressure of 200 to 2000 psig and a feed rate of 0.05 to 0.80 GPH/lb. of catalyst, fractionating the dimer product to obtain a fraction boiling at at least 500°F., alkylating benzene with said high boiling dimer fraction in the presence of a Friedel-Crafts catalyst, thereafter segregating from the resulting alkyl benzene a heavy alkylate fraction having an initial boiling point of at least 640°F., subjecting said heavy alkylate fraction to sulfonation and converting the sulfonated product to an alkaline earth metal salt. The salts thus prepared have been

found to be superior in heavy duty engine performance to similar alkaline earth metal salts of the same molecular weight prepared from sulfonated detergent alkylate bottoms.

- 5 The  $C_3$  to  $C_{16}$  monoolefins can be selectively dimerized and/or codimerized to  $C_{10}$  to  $C_{30}$  monoolefins in the presence of a silica-alumina catalyst and household detergents can be prepared by alkylating benzene with selected fractions of the dimer and/or codimer olefins, so prepared, sulfonating and neutralizing to obtain alkyl benzene sulfonate detergents. One preferred embodiment relates to dimerizing a  $C_3$  to  $C_{12}$  olefin, obtained as a byproduct in the

commercial preparation of tetrapropylene for tetrapropylenebenzene detergents. This commercial preparation of tetrapropylene is usually done by reacting propylene in the presence of a phosphoric acid catalyst. The phosphoric acid is usually supported on kieselguhr.

While it is not intended to limit the invention by any theory it is postulated that in the inventive process the active sites on the catalyst are so spaced with relation to the length of the chain of the feed olefin that growth type polymerization is obtained. This dimerization may be represented, for example, by the following equation:



(The dashed or dotted lines merely indicate carbon positions)

- 30 It is further postulated that the dimerized olefin has an internal double bond, which is stabilized by the methyl group, so that on alkylation only specific alkylate isomers are obtained. Thus, on alkylation the phenyl group will be attached on carbons 1, 2, or 3, preferably 3 when the double bond joins carbons 1 and 2, producing alkyl benzene sulfonate detergents which are biodegradable.

- 35 The feed stock for the production of dimerized olefins for superior higher molecular weight detergents in accordance with the present invention will be the low boiling polymer from a conventional phosphoric-acid-on-kieselguhr polymerization process. While  $C_3$  to  $C_{13}$  olefins are useful in the process of the present invention, particularly useful are a  $C_3$  to  $400^\circ\text{F}$ . cut, predominantly  $C_3$  olefins, and a  $360^\circ$  to  $400^\circ\text{F}$ . cut, predominantly  $C_{12}$  olefins:  $C_3$  to  $500^\circ\text{F}$ . olefins can also be used. 50 It is to be noted that these byproduct materials from the conventional process are of little value other than as fuels and that recycle of these materials in the conventional phosphoric-acid-on-kieselguhr process does not appreciably increase the yield of the  $C_{13}$  and higher materials.

- 55 The silica-alumina catalysts which are used in the present process and contain a weight ratio of silica to alumina of 1:1 to 15:1 preferably contain from 50 to 90% silica and from 50 to 10% alumina. In addition, small amounts, i.e. not more than 10%, of other metal oxides, such as iron and nickel, may be present but are only coincidental in the success 65 of the present process. These catalysts may be

prepared by methods well known in the art, such as by impregnating silica with alumina salts, by directly combining precipitated hydrated alumina and silica or by joint precipitation of alumina and silica from aqueous solutions of these salts. Following this initial step in its preparation, the catalyst is washed and dried and then heated to activate it. This latter heating step ensures that the desired structure and acidity of the catalyst will be obtained for optimum activity and selectivity in the process. Thus, the catalyst is heated at temperatures in the range of  $300$  to  $1500^\circ\text{F}$ ., preferably  $900$  to  $1100^\circ\text{F}$ ., e.g.  $1000^\circ\text{F}$ ., preferably with hot air for times in the range of  $1/2$  to 25 hours, preferably 1 to 3 hours, e.g. 2 hours. Surface areas of above  $350 \text{ M } 2/\text{g}$ , e.g.  $500 \text{ M } 2/\text{g}$  are obtained. It should be noted that these catalysts do not include the molecular sieve catalysts.

The catalyst may be used either in the form of pellets for fixed or moving bed processes or in the form of powder for fluidized operations. Where the catalyst is used in the form of pellets, these catalysts may be prepared by pelleting to form preferably  $1/8''$  to  $1/2''$  pellets, e.g.  $3/16''$  pellets, followed by heating as previously described to activate the catalyst.

The silica-alumina catalysts used in this invention are preferably fresh catalysts but in addition may less preferably be "spent" or "equilibrium" cracking catalysts which have been used in the cracking of hydrocarbons, e.g. gas oils, to produce lower boiling materials. In these processes activity of the catalyst progressively decreases due to the accumulation

- of coke and other materials thereon. Such catalysts are ordinarily continuously regenerated in the process by burning off the deposited coke at temperatures usually of less than about 1150°F., e.g. 950—F., in a stream of air which may be diluted with an inert gas in order to control the rate of burning. Regeneration processes, however, do not completely restore the catalyst to its original activity, so that regeneration becomes progressively less effective. This results in part from the deposition of foreign materials, principally metals or metal compounds, on the catalyst which are not removed in the regeneration process. Additionally, the surface area of the catalyst progressively decreases. When the cracking activity after regeneration has decreased from 70 to 50% of its original activity, regeneration thereof is no longer feasible and the catalyst is referred to as "spent catalyst" and is discarded. Such catalysts ordinarily have surface areas of about 100 M<sup>2</sup>/g, which surface areas are, of course, far below optimum for the present process. Catalyst having an activity of above 50 to 70% of original activity are referred as "equilibrium" catalysts and these catalysts may be used in the process (although of course surface area for these catalysts also will be low). A typical spent catalyst containing 87% SiO<sub>2</sub> and 13% Al<sub>2</sub>O<sub>3</sub> when fresh, may contain, when "spent", 1 to 5% iron and 0 to 1% nickel as impurities. In this invention, however, the amount and nature of the metallic impurities are of little consequence.
- According to the present invention, reaction conditions in the dimerization and/or codimerization should include temperatures in the range of 200 to 500°F., preferably 350 to 450°F., e.g. 400°F., pressures of 200 to 2000 psig, preferably 500 to 1000 psig, e.g. 800 psig, space velocities of 0.05 to 0.80 GPH/lb. of catalyst, preferably 0.08 to 0.50 GPH/lb. of catalyst, e.g. 0.12 or 0.20 GPH/lb. of catalyst. In a preferred embodiment, the feed contains less than 0.01 mol % of water, preferably less than 0.007 mol % water, e.g. 0.004 mol % water. This may be obtained if necessary by drying the feed and / or catalyst after regeneration.
- The catalyst will ordinarily be regenerated after a catalyst life of about 50 to 100 gallons of net polymer/lb. of catalyst, preferably about 60 to 80 gallons of net polymer/lb. of catalyst, e.g. 75 gallons of net polymer/lb. of catalyst. This regeneration is conducted at temperatures in the range of 800 to 1500°F., preferably 900 to 1200°F., e.g. 1000°F. for contacting times of 2 to 20 hours, preferably 5 to 10 hours, e.g. 8 hours. Shorter times are, of course, used with the higher temperatures. This contacting is preferably conducted in the presence of an inert gas and, if it is desired to burn off carbon, also in the presence of air. The temperatures described above are desirable in order to obtain the preferred struc-
- ture of the catalyst following regeneration.
- Alkylation is carried out utilizing benzene in the presence of a Friedel-Crafts type catalyst, suitably at temperatures in the range of 15 to 160°F., e.g. 40°F. for times of 5 to 60 minutes, e.g. 18 minutes. Suitable catalysts include, for example, AlCl<sub>3</sub>, HF, BF<sub>3</sub> and AlBr<sub>3</sub>, polyphosphoric acid, H<sub>2</sub>SO<sub>4</sub> and aluminum chloride hydrocarbon complexes. Aluminum chloride is the preferred catalyst, which may be either fresh AlCl<sub>3</sub> or spent AlCl<sub>3</sub> sludge from a previously alkylation step, fortified by the addition of 5 to 20 wt. % of fresh AlCl<sub>3</sub>.
- The feed olefin for the alkylation reaction is obtained by fractionation from the product of dimerization and/or codimerization. This feed boils at at least 500°F., the upper boiling point not being critical.
- It is generally desirable to maintain in the reaction mixture a volume ratio of aromatic hydrocarbon to olefin of at least 3:1, e.g. 5:1, although ratios up to 20:1 may be used.
- Although temperatures during alkylation with AlCl<sub>3</sub> can range as high as 140°F., it is preferred to use temperatures of between 20 and 80°F., e.g. 40 or 50°F. Weight ratios of olefin to catalyst will be in the range of 30:1 to 7:1, e.g. 20:1 or 10:1. Additionally, in the case of the use of aluminum chloride, an activator such as HCl can be added in an amount of from 15 to 40 wt. %, e.g. 20 wt. %, based on aluminum chloride.
- If a liquid hydrogen fluoride catalyst is used for alkylation, it is preferred to use an acid-to-hydrocarbon reactants volume ratio of 0.1:1 to 1.0:1, e.g. 0.3:1 and temperatures in the range of 30 to 60°F., e.g. 50°F. The concentration of this catalyst can range from 85% to 100% HF by weight, its water content being maintained very low, e.g. no higher than 1 or 2% by weight, the remainder being dissolved hydrocarbon material.
- The alkylated aromatic fraction is recovered from the alkylation reaction mass and is sulfonated in known manner, e.g. by contact with an excess of concentrated sulfuric acid, oleum, ClSO<sub>3</sub>H, sulfur trioxide, and the like. For the production of satisfactory oil-soluble metal sulfonates for the present invention the alkylate fraction having an initial boiling point of at least 640°F. is sulfonated. A typical alkylate has an initial boiling point of 650°F., 5 liquid per cent distilling off at 658°F., 10% off at 670°F., 30% off at 694°F., 50% off at 722°F., 70% off at 755°F., 90% off at 830°F., 95% off at 870°F., and final boiling point above 990°F. The sulfonation can be carried out at temperatures up to 140°F., preferably for oleum 60 to 140°F., e.g. 120°F. The acid concentration is preferably at least 97%. Acid up to 100% concentration and preferably oleum containing up to e.g. 20 wt % SO<sub>3</sub> or higher, can be employed. With higher acid concentration, lower reaction times are

acid, about 2 hours with 100% acid, and preferably 0.5 to 1 hour, e.g. 0.7 hour, with oleum. Volume ratios of sulfuric acid to hydrocarbon can range from 0.8:1 to 1.25:1, a 1:1 ratio being suitable.

The sulfonation product mixture can be separated by "layering" to remove part of the excess spent acid before neutralizing or it can be neutralized directly. When neutralized the sulfonic acids are thus converted to sulfonic acid salts and the excess sulfuric acid into sulfate. The sulfate normally settles out, and its complete removal is effected by filtration. If necessary, any sludge that forms during sulfonation that cannot be removed by simple settling can be removed by treating the product with a filter aid such as diatomaceous earth. Also, if it is found necessary, the sulfonic acids can be blown with nitrogen to remove  $\text{SO}_2$ .

To prepare the alkaline earth metal salts, the sulfonic acids can be neutralized directly with an alkaline earth metal base such as  $\text{BaCO}_3$  or  $\text{Ca(OH)}_2$ , although more usually the sodium or other alkali metal salt is first formed (e.g. by neutralization with  $\text{Na}_2\text{CO}_3$ ), followed by conversion to alkaline earth metal salt by double decomposition. The neutralization is generally carried out by contact with basic aqueous solution at temperatures of from 65 to 160°F., those between 80 and 125°F., e.g. 100°F., being preferred.

Conversion of alkali metal salts to alkaline earth metal salts by double decomposition can be accomplished by reacting the alkali metal sulfonate with an alkaline earth metal salt, such as the chloride.

Double decomposition of the alkali metal sulfonates with aqueous solutions of salts of the desired alkaline earth metal can conveniently be carried out using an aqueous alcohol solution of the sulfonate. Thus, for example, a 10 to 30% aqueous solution of an alkaline earth metal salt, in an amount 10 to 200% in excess of the theoretical amount required, is well mixed with the alkali metal sulfonate solution at substantially atmospheric temperature. The alkaline earth sulfonate, containing some alkali metal sulfonate, salts, and water, precipitates as a curdy mass. This mass can be fluxed with lubricating oil, dehydrated by heating to 275 to 325°F., and filtered free of insoluble material. Alternatively, the alkali metal sulfonate solution and a 10 to 30% aqueous solution of alkaline earth metal salt in 10 to 200% excess of theoretical can be emulsified with the oil in which the sulfonate will be dissolved to form the desired sulfonate concentrate. In some cases a small amount of the alkaline earth hydroxide can also be incorporated to maintain alkalinity. The mixture is then heated to 275 to 325°F. to drive off the water and the pro-

duct filtered to remove insoluble salts.

Still another alternate method is to dissolve the sodium sulfonate in a mineral oil base in a concentration equivalent to that desired for the alkaline earth metal sulfonate and then emulsify the oil solution with an aqueous solution of an alkaline earth metal inorganic salt such as calcium chloride. As in the other double decomposition methods, an excess of the inorganic acid salt is used and the double decomposition is effected at a temperature of about 100 to 200°F. The reaction takes place rapidly, and the emulsion can then be permitted to settle. The separated oil layer can then be heated to 300°F. or higher to effect dehydration, after which the oil solution of the alkaline earth metal sulfonate can be filtered.

Concentrates prepared in accordance with this invention will comprise a mineral lubricating oil to which has been added from 10 to 80 wt %, or more, usually from about 30 to 60 wt. % of the alkaline earth metal sulfonate.

The alkaline earth metal sulfonates prepared in accordance with this invention can be added to lubricating compositions in concentrations ranging from 0.1 to 10 wt. %, or more usually in concentrations of from 0.4 to 5 wt. %. The lubricating oils include not only mineral lubricating oils but also synthetic oils including synthetic hydrocarbons, dibasic acid esters, such as di-2-ethylhexyl sebacate, carbonate esters, phosphate esters, polysilicones, and polyglycols. The lubricant compositions may also contain other additives such as dyes, pour point depressants, e.g. wax alkylated naphthalene, antiwear agents such as zinc dialkyl dithiophosphates, antioxidants such as phenyl alpha naphthylamine, other inhibitors such as alkyl phenol thioethers or their metal salts, such as barium octyl phenol sulfide, viscosity index improvers such as polyisobutylene, and so forth.

It is within the contemplation of this invention to prepare additive concentrates having from 10 to 80 wt. % of additives, the balance being mineral oil, for convenience in handling.

#### EXAMPLE 1

##### Part A — Preparation of Olefin Dimer

Using as the feed stock a light polymer fraction having  $\text{C}_6$  olefins and higher up to a final boiling point of 400°F., said polymer having been obtained by polymerizing propylene with a catalyst comprising phosphoric acid on kieselguhr (UOP catalyst), several runs were made in which the feed was contacted with silica-alumina catalyst at temperatures ranging from 360 to 400°F. and pressures of from 500 to 2000 psig. The conditions of each run and the product distribution of the dimer thereby obtained are given in Table I.

TABLE I

## Dimerization of Light Polymer Over Silica-Alumina Catalyst

Catalyst: 12%  $\text{Al}_2\text{O}_3$  — 88%  $\text{SiO}_2$ Feed: Propylene UOP light polymer, boiling  $\text{C}_5$  — 400°F.

Run No.	1	2	3	4	5	6
Temperature, °F.	400	400	400	360	400	360
Pressure, psig	800	800	800	1500	500	500
Space Velocity GPH/lb.	0.12	0.25	0.37	0.12	0.12	0.12
Product Distribution Liquid Vol. %						
$\text{C}_5$ — 400°F.	45	52	62	47	52	56
400 — 500°F.	12	11	11	10	11	10
500°F. +	43	37	27	43	37	34

*Part B — Preparation of Alkylate*

5 An olefin fraction having an initial boiling point of 500°F. and prepared in the manner of Run 5 of Example 1 was used to alkylate benzene with fresh aluminum chloride catalyst in the presence of HCl to maintain catalyst

activity. The extent of reaction was followed by measuring bromine numbers and running the reaction until the bromine number was 10 below 0.5. The reaction conditions and the product yields are given in Table II.

TABLE II

## Alkylation of Benzene With Heavy Olefins

Run	A
Benzene/olefin, volume	4/1
Temperature, °F.	50
$\text{AlCl}_3$ , wt. % on olefin	8
Product yield, LV% on olefin (liquid vol. % based on olefin)	
Light alkylate, 200 to 650°F.	32
Heavy alkylate, 650°F. +	73
Total	105

## EXAMPLE 2

15 *Part A — Preparation of Dimer of UOP Tetrapropylene*

Using as feed stock a 360—400°F. UOP polymer fraction, said polymer having been obtained by polymerizing propylene with UOP

20 catalyst, several runs were made in which the feed was contacted with the silica- alumina catalyst used in Example 1. The conditions of each run and product composition are shown in Table III.

TABLE III

Dimerization of UOP Tetrapropylene Fraction Over Silica-Alumina Catalyst

Run No.	7	8	9
Temperature, °F.	400	400	400
Pressure, psig.	200	800	1500
Space velocity V/V/Hr.	1	1	1
Product Distribution, Vol. %			
Unconverted feed	70	58	54
400 — 500°F. fraction	10	10	10
500°F.+ Fraction	20	32	36

*Part B*

Using the tetrapropylene dimer, boiling above 500°F., prepared as in Run 9, benzene was alkylated in the presence of aluminum chloride using a benzene to olefin volume ratio of 4:1 and a temperature in the range of 50 to 90°F. The reaction conditions, the alkylate yield data, and the alkylate distribution data for three separate runs are given in Table IV.

TABLE IV

Alkylation of Heavy Olefins

Run	B	C	D
Olefin feed source	UOP tetrapropylene dimer, 500°F.+		
Alkylation conditions			
Temperature, °F.	90	90	50
Benzene/olefin volume ratio	4/1	4/1	4/1
AlCl <sub>3</sub> , wt. % on olefin	7.1	6.9	6.4
Total alkylate distribution, L.V. %			
200 — 500°F.	9	8	8
500 — 650°F.	20	19	16
650°F.+	71	73	76
Alkylate yield on olefin, L.V. %			
200 — 500°F.	10	9	8
500 — 650°F.	21	21	17
650°F.+	75	81	82
Total	106	111	107

## EXAMPLE 3

A portion of the olefin dimer prepared as in Run 4, Example 1 is used to alkylate benzene

in the presence of an  $\text{AlCl}_3$ -HCl catalyst. Alkylation conditions are:

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$\text{AlCl}_3$ addition rate	—	8 wt. % on olefin
HCl addition rate	—	20 wt. % on $\text{AlCl}_3$
Benzene/Olefin volume ratio	—	4 : 1
Reactor Temperature	—	50° F.

10 The alkylates obtained are sulfonated with 20% oleum at 60° to 140°F. by adding the oleum to the alkylate. The weight ratio of oleum to hydrocarbon is 1.4:1 and the materials are reacted for 45 minutes. Following reaction, the sulfonation product mixture is neutralized to a pH of 7 with 30% aqueous sodium hydroxide to obtain the sodium salts of the sulfonic acids admixed with sulfates produced from excess spent sulfuric acid. The neutralization is carried out at a temperature of about 115°F. utilizing a reaction time of about 15 minutes. The sodium salts are converted to calcium salts by double decomposition with calcium chloride.

## EXAMPLE 4

## Part A — Preparation of Alkylate

Using in one case a dimer of a predom-

25 antly  $\text{C}_8$  olefin prepared as described in Example 1, run no. 5, and in a second case a dimer of essentially  $\text{C}_{12}$  olefins obtained as described in Example 2, run no. 8, and taking in each case the entire fraction boiling above 500°F., benzene was alkylated with each fraction using aluminum chloride catalyst. The alkylation conditions were 4/1 benzene to olefin ratio, 50—80°F. temperature and 8 wt. %  $\text{AlCl}_3$  on olefin. The characteristics of the heavy alkylate thereby obtained in each case are given in Table V, along with the characteristics of a heavy alkylate identified as detergent alkylate bottoms, these bottoms being the fraction boiling at 650°F. and higher obtained as a byproduct in making detergent alkylate by alkylating benzene with tetrapropylene obtained by polymerizing propylene with phosphoric acid catalyst.

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TABLE V  
Heavy Alkylate Quality

	Alkylate A	Alkylate B	Conventional Detergent Alkylate Bottoms
Olefin feed	C <sub>3</sub> —400°F.	360—400°F.	
Main componentn	C <sub>9</sub>	C <sub>12</sub>	
Olefin boiling range used for alkylation	500°F.+	500°F.+	
Heavy alkylate properties			
Boiling range, °F.	650°F.+	650°F.+	650°F.+
Viscosity at 100°F., SUS	350	615	419
Aniline point, °F.	143	150	146
Distribution of side chain by mass spectrometer, mol %			
below C <sub>16</sub>	5	6	11
C <sub>16</sub> — C <sub>17</sub>	8	8	12
C <sub>18</sub>	13	8	5
C <sub>19</sub> — C <sub>23</sub>	47	26	28
C <sub>24</sub>	6	23	14
above C <sub>24</sub>	21	29	30
Average carbon number of total alkylate	27.3	28.3	28.1
Average molecular weight	376	391	388

It will be seen from the information in Table V that the average molecular weight, the average carbon number of the total alkylate, and the distribution of side chains in products made in accordance with the present invention are quite similar to those of a typical detergent alkylate bottoms.

*Part B — Preparation of Sulfonate*

Each of the alkylates that was prepared as described in Part A of this example was sulfonated with SO<sub>3</sub> in the following manner. The alkylate was mixed with an equal volume of hexane and then while the mixture was heated under reflux at about 100°F., SO<sub>3</sub> in a nitrogen carrier stream (5% SO<sub>3</sub>) was bubbled through the hexane-alkylate mixture until a total ratio of SO<sub>3</sub> to alkylate of 1.1 to 1 was

attained. The rate of SO<sub>3</sub> addition was in the range of 0.08 to 0.14 grams of SO<sub>3</sub> per gram of alkylate per hour. At the end of the sulfonation treat, the hexane was stripped off by bubbling nitrogen through the mixture at 125°F. over a period of about two hours. The sulfonic acid mixture thereby obtained was then converted to sodium salts by pouring the mixture into a 10% solution of sodium hydroxide in a mixture of 30% ethanol and 70% water, the amount of sodium hydroxide being slightly more than the calculated amount needed to neutralize the sulfonic acids. Neutralization temperature was about 120°F. In each case, it was found that about 7 wt. % of unsulfonated hydrocarbon was present.

The sodium sulfonates thus formed were mixed with a light mineral lubricating oil in



- a proportion calculated to give about a 45% concentrate of the ultimate calcium sulfonate in oil, after which the water and alcohol were driven off by heating. Then in each case the oil solution of sodium sulfonate was emulsified with a saturated solution of calcium chloride, the amount of calcium chloride used being about 2.5 to 3 equivalents of calcium per equivalent of sodium. The emulsion was formed by stirring the mixture at 190 to 200°F. Reaction took place within 15 to 20 minutes. The emulsion was then allowed to settle and the aqueous layer was drawn off, after which a small amount of slaked lime, i.e.,  $\text{Ca}(\text{OH})_2$  was added with stirring at ambient temperatures. The amount of lime was about 0.5 equivalent per equivalent of calcium sulfonate. The mixture was then heated to 300°F. to drive off water and the resulting calcium sulfonate concentrate in oil was filtered through diatomaceous earth. The concentrate contained about 45 wt. % of the calcium sulfonate.
- Example 5 — Testing of Oil Blends*
- Comparative oil blends were prepared to evaluate the sulfonates of the present invention as dispersant components in a balanced blend of dispersant components and alkalinity-contributing components in an oil composition designed for severe service in a diesel engine. Each blend was prepared by simple mixing of 14 vol. % of an additive concentrate blend with 86 vol. % of a refined, high viscosity index paraffinic lubricating oil of SAE 30 viscosity grade. The additive concentrate blend was prepared by simple mixing of four additives, each of which was in turn a concentrate in mineral lubricating oil. The concentrate blend consisted of 16 vol. % of mixed barium-calcium nonyl phenol sulfide concentrate (35 wt. % in oil), 9 vol. % of barium nonyl phenate concentrate (50 wt. % in oil), 5 vol. % of an oil concentrate of a 300 base number calcium synthetic hydrocarbon sulfonate (28 wt. % sulfonate, 24 wt. %  $\text{CaCO}_3$ , in oil), and 70 vol. % of the sulfonate concentrate being evaluated in the test (45 wt. % in oil). The purpose of the metal phenol sulfide was to impart an inhibitor function to the oil, while the overbased sulfonate and the metal phenate ensured that the oil would have sufficient reserve alkalinity. It is to be noted that of the total sulfonate in the blend for each 96 parts of the sulfonate being evaluated, there were only about 4 parts of the alkalinity-contributing sulfonate.
- Each of the comparative blends thus prepared was subjected to the 240-hour Caterpillar 1—G Test, which is a test that is used to certify military Series 3 lubricants for the Caterpillar diesel engine. This test is fully described in the Caterpillar Test Manual. At the end of each test the engine is dismantled and inspected for deposits. The most significant rating is that of the engine piston. A merit rating is used in which a value of 100 signifies a perfectly clean piston, and a value of 0 signifies a completely dirty piston. The results obtained in these tests are given in the following Table VI. A comparative test was run with the calcium salt of the sulfonated product of the detergent alkylate bottoms referred to in Table V.

TABLE VI

Caterpillar Engine Test Data Test 1—G, 240 Hours

Alkyl Benzene Source	$\text{C}_9$ Dimer	$\text{C}_{12}$ Dimer	Detergent Alkylate Bottoms
Piston merits <sup>(1)</sup>	90	98	60

<sup>(1)</sup> Best = 100

- It will be noted that in the Caterpillar Engine Test each of the calcium sulfonates prepared in accordance with the present invention gave a much cleaner piston than did the prior art calcium salt of sulfonated detergent alkylate bottoms.
- WHAT WE CLAIM IS:—**
1. A process for preparing an oil-soluble alkaline earth metal hydrocarbon sulfonate which comprises the steps of dimerizing a monoolefin fraction in the  $\text{C}_6$  to  $\text{C}_{15}$  range by contacting said fraction with an activated silica-alumina catalyst having a silica-to-alumina weight ratio of from 1:1 to 15:1, said contacting being conducted at a temperature in the range of 200 to 500°F at a pressure of 200 to 2000 psig and a feed rate of 0.05 to 0.80 GPH/lb. of catalyst, fractionating the dimer product to obtain a fraction boiling at at least 500°F., alkylating benzene with said high boiling dimer fraction in the presence of a Friedel-Crafts catalyst, thereafter segregating from the resulting alkyl benzene a heavy alkylate fraction having an initial boiling point of at least 640°F., subjecting said heavy alkylate fraction to sulfonation and converting

- the sulfonated product to an alkaline earth metal salt.
2. A process according to claim 1 in which the olefin fraction is a  $C_3$  to 400°F cut.
- 5 3. A process according to claim 1 or claim 2 in which the olefin fraction comprises predominantly  $C_3$  olefins.
4. A process according to claim 1 in which the olefin fraction is a 360—400°F. cut.
- 10 5. A process according to claim 4 in which the olefin fraction comprises predominantly  $C_{12}$  olefins.
6. A process according to claim 1 in which the olefin fraction is a  $C_6$  to 500°F cut.
- 15 7. A process according to any preceding claim in which the said olefin fraction is derived by polymerizing propylene in the presence of a catalyst comprising phosphoric acid on kieselguhr.
- 20 8. A process according to any preceding claim in which an alkali metal salt of the sulfonated heavy alkylate fraction is formed after sulfonation, and the said alkaline earth metal salt is formed therefrom by a double
- 25 decomposition reaction.
9. A process according to claim 1 substantially as hereinbefore described.
10. A process for preparing an oil soluble alkaline earth metal hydrocarbon sulfonate substantially as hereinbefore described with reference to the Examples.
11. An alkaline earth metal sulfonate prepared by the method of any of claims 1 to 10.
12. An alkaline earth metal sulfonate according to claim 11 in which the alkaline earth metal is calcium.
13. A concentrate comprising a mineral lubricating oil to which has been added from 10 to 80 wt.% of an alkaline earth metal sulfonate in accordance with claim 11 or claim 12.
14. A lubricating oil composition comprising a major proportion of a mineral lubricating oil and from 0.1 to 10 wt.% of an alkaline earth metal sulfonate in accordance with claim 11 or claim 12.
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